

A NEW TANNAGE
TETRAKIS (HYDROXYMETHYL) PHOSPHONIUM
CHLORIDE-RESORCINOL*

ABSTRACT

Tetrakis(hydroxymethyl)phosphonium chloride (THPC) and resorcinol react under mildly alkaline conditions to form tanning compounds. These can be generated in the presence of collagen to give an *in situ* tannage. The leather is characterized by a light color and a high hydrothermal stability. Procedures are given for tanning with THPC and resorcinol as the only tanning agents and for their use in a combination tannage with basic chromium sulfate. Several kinds of sheepskins were tanned on an experimental tannery scale. These were processed into suede and grain garment, lining, and work glove leathers in tanneries.

An hypothesis is proposed to explain the structures of the tanning agents, their reaction with collagen, and the inability to tan under acidic conditions.



INTRODUCTION

This paper describes a new *in situ* tannage using tetrakis(hydroxymethyl)-phosphonium chloride (THPC) and resorcinol (1). These compounds react under alkaline conditions in the presence of the skin to yield leather with a high hydrothermal stability.

THPC has been used alone for tanning (2). The leather was thin and firm and had a shrink test of 80°-85°C.

Resorcinol has been used with formaldehyde to produce commercial leather by an *in situ* tannage (3). Leather resistant to boiling water has been made, and a Mannich-type mechanism of tanning was postulated.

The structure of THPC suggested that it might react with resorcinol under mild conditions to form tanning compounds. This proved to be the case. The tannage is capable of producing leather of commercial quality and is also of interest from a scientific standpoint.

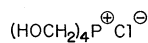
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†Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

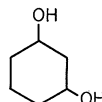
PROCEDURE

Many runs of several skins each have been made in the laboratory to work out the details of the tannage and apply it to different kinds of raw stock and leathers. Most of the work was done on sheepskins for convenience and economy. Two procedures will be outlined, one using THPC and resorcinol as the only tanning materials, the other a low THPC-resorcinol tannage followed by a chrome retannage.

The formulas of the compounds used are as follows:



THPC



Resorcinol

THPC-resorcinol tannage.—The following procedure was run on three domestic sheepskins in a small drum. The percent of chemicals is based on the drained pickle weight of the skins.

Pickled skins, degreased	100 %
Water	100 %
Sodium sulfate, anhydrous	10 %
Sodium acetate	2.0%
Resorcinol	2.5%
Tetrakis(hydroxymethyl)phosphonium chloride	4.3%
Run 1½ hr.; pH 4.2; temperature 27°C.	
Sodium carbonate	2.5%
Water	25 %
Run 1½ hr.; pH 6.0; temperature 27°C.	
Sodium carbonate	2.5%
Water	25 %
Run 1½ hr.; pH 8.7; temperature 27°C.; Ts 88°–90°C.	
Run 2 hr.; pH 8.8; temperature 28°C.; Ts 90°–92°C.	
Wash 30 min.	
Formic acid	1.5%
Sulfuric acid	0.6%
Water	100 %
Run 30 min.; pH 3.4; Ts 90°–92°C.	
Wash 30 min.	

All the initial chemicals were added at one time. The skins were entered after the chemicals were dissolved. The load was warmed cautiously with steam after 5 hr. of tanning to imitate the build-up of heat in a large drum. This does hasten the tanning and increases the shrink temperature. In this run there was only a slight rise in temperature, but many runs were raised to 38°–43°C. For convenience in a small load a total liquor ratio of 150% was used. When more than 100% liquor is used, the sodium sulfate should be on a solution basis. Part of the water was withheld to dissolve the sodium carbonate and rinse it into the drum through the gudgeon. The pH was raised gradually. Tanning was started at a pH of 4.0–4.5, at which THPC alone has a tanning action. The pH was then raised to 6.0–6.5 to increase the rate of tanning. Tanning was completed at a pH of 8.5–9.0. A mole-to-mole ratio of THPC and resorcinol was found to be satisfactory.

After 6 hr. a sample of the liquor was tested for the presence of resorcinol by adding formaldehyde and concentrated sulfuric acid. A red precipitate of a resorcinol-formaldehyde polymer is formed if the skins have not taken up all of the resorcinol. In this procedure there was a small amount of precipitate. However, in the interest of completing the tannage during the day, tanning was discontinued. The skins could be left in the drum overnight with a moderate increase in shrink temperature and fullness, but streaks of color would form on the grain. A small amount of THPC also remains in the liquor, judging by the characteristic smell of this compound.

The leather was processed into slipper leather in a tannery with the regular production and was judged to be of standard commercial quality.

THPC-resorcinol tanning—chrome retanning.—To explore the possibilities of the tannage and to lower its cost, a number of combination tannages were run with varying amounts of tanning materials. These included basic chromium and zirconium sulfates, wattle, canaigre, and methylolmelamine. For simplicity, only the combination with chrome will be described.

Eight New Zealand lambskins were tanned with 0.85% THPC and 0.5% resorcinol. The procedure was the same as given above. After 6 hr. of tanning the pH of the liquor, in this instance, was 9.2, and the shrink temperature of the skins was 80°C. Only a trace of resorcinol remained in the liquor, which gave a pink-colored solution but no precipitate upon the addition of formaldehyde and sulfuric acid. The skins were washed, acidified, washed, and horsed overnight.

The next day the skins were retanned with 3% of a one-bath chrome tan given in two feeds and run for a total of 6 hr. The pH of the liquor was 3.9, and the leather withstood boiling water for 3 min. before shrinking. The shrink test was the same 2 hr. earlier, and the retannage could probably have been discontinued at that time.

The leather was processed into suede garment leather in a tannery. The quality of the suede was excellent and commercially acceptable.

Both procedures have been used to produce a range of finished leathers from both wool and hair sheep. Domestic sheepskins have been processed into work glove and lining leathers in addition to the slipper leather mentioned previously. Grain garment leather was made from Iranian, Turkish, and Syrian sheepskins.

Properties of the leather.—Leather tanned with THPC and resorcinol has many of the properties of vegetable-tanned leather, which is not surprising in view of the phenolic nature of the tanning material. The leather is full, round, and mellow. The color after tanning and acidifying is off-white to light tan, depending on such factors as pH, temperature, and time. The leather is surprisingly light-resistant for a phenolic tannage, changing only slowly. The color is lighter and more resistant to change than the resorcinol-formaldehyde tannage. The hydrothermal stability is high. Sheepskin leather which does not shrink in boiling water can be obtained, but the skins are then somewhat overtanned and lower in strength than desired. Leather with a shrink test of 90°–95°C. has normal strength.

The THPC-resorcinol tannage has the interesting ability of preventing the afterglow of chrome-tanned leather. Of course, the oil in the leather burns first when the leather is ignited. When this is complete, the burning ceases. The reduction in flammability of fabrics by organic phosphorus compounds is well known in the textile industry and is a development of our Southern Regional Research and Development Division (4).

TABLE I

ANALYSIS OF THPC-RESORCINOL-TANNED FINISHED LEATHER

Sheep	Amount THPC Used*	Phosphorus		
		Schoniger	Carius	Chlorine
Iranian	none	0.09†	0.01	—
Domestic	0.87	0.34	0.20	0.09
Domestic	1.73	0.54	0.40	0.08
New Zealand	1.73	0.46	0.40	0.07
Iranian	1.73	0.47	0.42	0.00
Domestic	2.60	0.67	0.56	0.21
Iranian	5.60	2.16	2.15	0.05

*Percent based on drained pickled weight.

†P and Cl expressed as percent on a moisture-free basis.

Our laboratory has been interested for sometime in the perspiration resistance of leather. The THPC-resorcinol-tanned leather exhibited a high degree of resistance to deterioration from perspiration. A detailed report on the evaluation of this property will be given in a separate paper.

Table I shows analyses of THPC-resorcinol leather for phosphorus (7) and chlorine. This substantiates that phosphorus-containing compounds are fixed by the collagen and that chlorine is eliminated during tanning. The figures should not be compared with one another since different procedures were used and the finished leather contained different amounts of oil. The trace of chlorine undoubtedly results from incomplete removal of sodium chloride during washing.

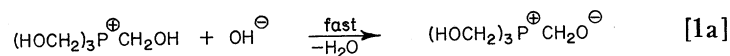
DISCUSSION

It is apparent that the tanning agents are polymers formed by the reaction of THPC and resorcinol. The molecular weights of the tanning molecules are probably relatively low in view of the mellow character of the leather, the insolubility of large molecules, and the interruption of the polymerization by reaction with collagen.

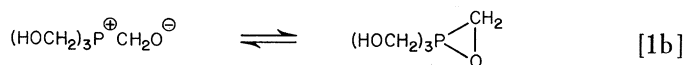
All the phenolic compounds evaluated appeared to react with THPC to form tanning agents, judging by the color of the leather. Phenol, catechol, hydroquinone, pyrogallol, gallic acid, and gentisic acid were tested with THPC. Under comparable conditions the hydrothermal stability of the leather was lower than that obtained with resorcinol, falling in the range of 80°–87°C. However, approximately the same shrink temperature can be obtained with THPC alone under the same conditions, so that the reactivity of phenols other than resorcinol and pyrogallol is somewhat difficult to assess. Resorcinol remains the preferred phenol from a technical standpoint.

A number of phosphorus compounds were tested with resorcinol. These were tris(hydroxymethyl)phosphine oxide, bis(hydroxymethyl)phosphinic acid, tris(1-aziridiny)phosphine sulfide, and tris(1-aziridiny)phosphine oxide. The results were entirely negative.

Unlike the tanning action of resorcinol and formaldehyde, tanning with THPC and phenols does not take place under acidic conditions. This is not surprising in view of the positive charge of the phosphonium moiety. This charge must be neutralized by hydroxyl ions in order to activate the methylol groups (5,6). A zwitterion is formed in accordance with equation 1a.

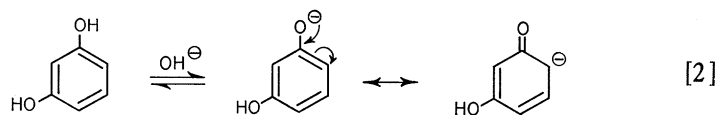


The zwitterion may also be written as a neutral phosphorane monomer, as in 1b.



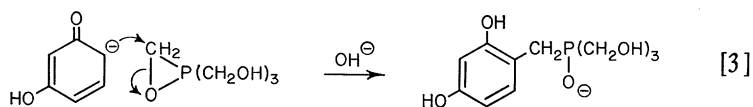
The phosphorane ring provides a logical pathway for reaction at the carbon atom.

Resorcinol in alkaline solution forms the phenoxide ion which resonates with the carbanion structure as shown in equation 2.

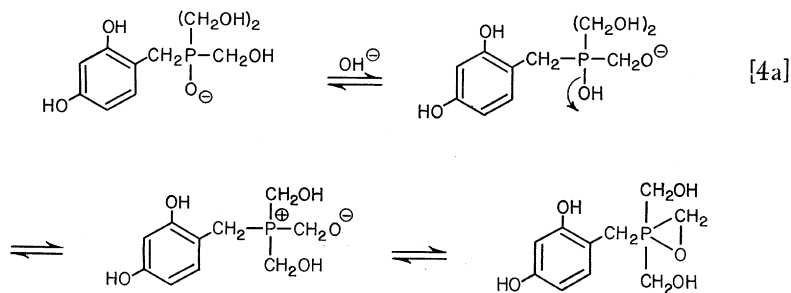


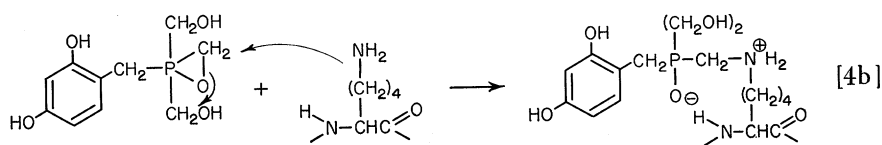
Resorcinol can, therefore, react by either oxygen or carbon alkylation. For simplicity, only carbon alkylation will be indicated.

The THPC and resorcinol are now in forms which will react with each other as in equation 3.



It seems likely that a second molecule of resorcinol and additional THPC react with this structure to form the simplest tanning molecule. However, for convenience, the above compound will be represented as reacting with collagen through another phosphorane ring, as in equations 4a and 4b.





Proton transfer to the oxygen anion would take place readily to yield the conventional substituted aminomethyl linkage with the ϵ -amino group of the lysine residue in collagen. Acidification regenerates the original positively charged phosphonium moiety in the form of a salt.

It appears reasonable to assume that steric hindrance would prevent the formation of additional phosphorane rings in the same molecule. If so, this would yield a linear polymer which is desirable and consistent with the properties of the leather.

The tanning molecule can continue to increase in length by reaction with additional resorcinol and THPC, utilizing the second very reactive position in the resorcinol molecule which is ortho to one hydroxyl group and para to the other. Polymerization is stopped by the competing reaction with the protein. Tanning molecules of relatively small size are indicated by the mellow character of the leather. The formation of strong covalent cross links between polypeptide chains would explain the high hydrothermal stability of the leather and may also account for its perspiration resistance (8).

SUMMARY

A new method of tanning, using tetrakis(hydroxymethyl)phosphonium chloride and resorcinol, has been described. Commercial quality leather possessing a high hydrothermal stability has been produced. An hypothesis to explain the mechanism of tanning has been proposed.

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